Chem. , 1987 , 238 :151
7 Vielstich W , Christersen P A , Weeks S A et al. Evidence for COH as an adsobed intermediate in anodic oxidation of methanol by ECDTM and SNIFTIRS. *J*. *Electroanal Chem*. , 1987 , 242 :327
8 Willsau J , Heitbaum J. MS detection of the hydrogen in methanol adsorbate. *J*. *Electroanal*. *Chem*. , 1985 , 185 :181
9 Wilhelm S , Vielstich W , Buschmann H W et al. Direct proof of the hydrogen in the methanol adsorbate at platinum ——an ECDTMS study. *J*. *Electroanal*. *Chem*. ,1987 , 229 :377
10 Fujihira M , Noguchi T. *Chemistry Letters* ,1992 :2 043
11 Willsau J , Wolter O , Heitbaum J. DOES the oxide layer take part in the oxygen evolution reaction on Pt. *J*. *Electroanal*. *Chem*. ,1985 , 195 :299
12 Hirata Y , Suga K , Fujihira M. *Chemistry Letters*. 1990 :1 155
13 Wolter O , Willsau J , Heitbaum J. Reaction pathways of the anodic oxidation of formic acid on Pt evidenced by ^{18}O labeling ——a DEMS study. *J*. *Electrochem*. *Soc*. ,1985 :1 635
14 Wohlfahrt-Mehrens M , Heitbaum J. *J*. *Electroanal*. *Chem*. , 1987 ,237 :251
15 Nishimura K , Machida K , Enyo M. On-line MS applied to Electroreduction of nitrite and nitrate ions of porous Pt electrode in sulfuric acid solutious. *Electrochim*. *Acta* , 1991 ,36 :877
16 Wloter O , Heitbaum J. *Ber*. *Bunsenges*. *Phys*. *Chem*. ,1984 , 88 :6
17 Santos E , Leiva E P M , Vielstich W et al. Comparative study of CO absorbates for different structures of platinum surfaces. *J*. *Electroanal*. *Chem*. ,1987 , 227 :199
18 Willsau J , Heitbaum J. *J*. *Electrochim*. *Acta* ,1996 , 31 :943
19 Hartung T , Baltruschat H. Differential Electrochemical MS using smooth electrodes adsorption and H/ D exchange reaction of Benzene on Pt. *Langmuir* ,1990 , 6 :953
20 Schmiemann U , Caltruschat H. The influence of the single-crystal orientation on the electrocatalytic hydrogenation of benzene and the H-D exchange. *J*. *Electroanal*. *Chem*. , 1993 , 347 :93
21 Schmiemann U , Jisys Z , Caltruschat H. The Electrochemical stability of inibitors. *Electrochimica Acta* , 1994 , 39(4) :561
22 Schmiemann U , Baltruschat H. The adsorption of ethene of Pt single crystal electrodes desorption products and observation of multiple adsorption states of DEMS. *J*. *Electroanal*. *Chem*. , 1992 , 340 :357
23 Kita H , Gao Y. *Catalysis Society of Japan*. , 1994 , 36(3) :210

差分电化学质谱法 (DEMS) 的回顾
II:DEMS 方法在某些电极反应中的应用

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摘要 本文第一部分〔电化学 ,1986 ,2(3)〕回顾了 DEMS 方法原理和发展 ,这里继续介绍 DEMS 方法的一些应用结果 ,如 CH_3OH ,HCOOH ,CO ,CO_2 ,NO_2^- ,NO_3^- 以及一些不饱和碳氢化合物的电化学氧化或还原研究.

关键词 电化学氧化 ,电化学还原 ,中间体 ,吸附

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A Review of Different Electrochemical Mass Spectroscopy(DEMS) Technique ①

II The Application of DEMS to some Electrode Processes

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In part I (See Electrochemistry, 1996, 9(3)), the development of DEMS has been reviewed. The following part is concerned about some experimental results obtained with the help of DEMS.

1 Applications of DEMS to the various electrode processes

1.1 CH_3OH electrooxidation

As we know at present, DEMS technique can give us an *in situ* analysis of products, intermediate species as well as information on their structure during the electrochemical reactions as a function of potential or time.

During the methanol electrooxidation at Pt electrode in sulfuric acid, several types of adsorbate have been usually assumed, for example, CO_{ad}[1], COH_{ad}[2], $(CO + COOH)_{ad}$[3] and $(HCO/COOH)_{ad}$[4]. Heitbaum and co-workers gave an identification of the methanol adsorbate by means of DEMS method. The results in Table 1 indicated clearly that one adsorbate needs three electrons in order to oxidize the adsorbed species formed during methanol oxidation. Therefore the intermediate was not CO_{ad}, which had been identified by vibrational spectroscopy[5], and COH_{ad} seemed to be the adsorbate. Iwasita and co-workers[6], using the on-line MS technique and labelled methanol, CD_3OH, found that adsorbate formed from CD_3OH did not contain a D atom, and deduced further that only COH_{ad} could be the adsorbed intermediate. Vielstich and Hamnett[7] also concluded that the intermediate was C-OH by Electrochemical Thermal Desorption Mass Spectroscopy (ECTDMS), which was supported by *in situ* IR studies of the oxidation process of CH_3OH on Pt.

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Besides the evidence of strong bound intermediate COH_{ad}, Heitbaum and Willsau[8] first gave the proof that intermediate contained hydrogen using electrochemical mass spectroscopy as in Figure 1, they concluded that the adsorbate of methanol was the formyl group: $(H-C=O)_{ad}$. Wilhelm and Iwasita, using ECTDMS technique, first proved the presence of hydrogen in the adsorbate during the methanol oxidation at Pt in H_2SO_4 solution[9].

Tab. 1 Results obtained in six different experiments for the determination of K^+ and the number of electrons, (n), released by the oxidation of the adsorbate of methanol to give product CO_2

Electrode No.	$10^3\ Q_1^{CO}/\ C$	$10^{10}\ Q_{M1}^{CO}/\ C$	$10^2\ K^*$	$10^3\ Q_1^{McOh}/\ C$	$10^{11}\ Q_{M1}^{McOH}/\ C$	n
1	3.39	1.42	8.37	3.01	8.41	3.0
1	3.48	1.37	7.87	3.12	8.49	2.9
1	3.60	1.44	8.00	3.20	8.52	3.0
2	4.30	3.23	15.0	2.30	11.5	3.0
3	4.13	2.48	12.0	2.41	9.32	3.1
3	4.27	2.92	13.7	2.07	9.78	2.9

1.2 CO_2 electroreduction

It is interesting in *in situ* DEMS detecting the electroreduction of CO_2 at gold in Na_2SO_4 aqueous solution as a function of the rotation speed[10]. The experimental results in Figure 2 show that the concomitant generation of gases, H_2 and CO could be recorded separately on mass spectra as a function of electrode potential. The mass signals of H_2 and CO with the sweep potential became sigmoidal with the increase of rotation speeds.

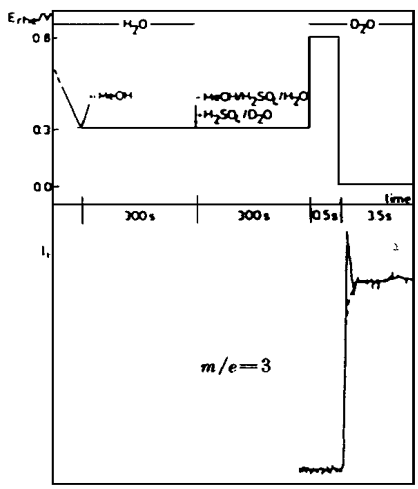

Fig. 1 Potential-time curve (top) and ion current of m/e = 3 response (bottom)

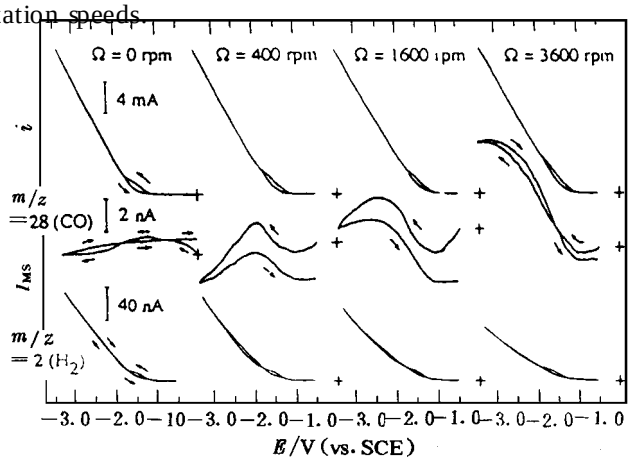

Fig. 2 Current (i) and mass signal intensity (I_{MS} as function (E) at different rotation speeds, electrolyte, 0.1 M Na_2SO_4 aqueous solution under CO_2 (pH 4.1 and 26 °C); woking electroed, gold porous thin film disk (8 mm in diameter) sputtered on the membrane; sweep rate, 5 mV s^{-1}

Wasmus and Vielstich[11] carried out a direct detection of volatile products formed during CO_2 electroreduction on different coppers by on-line mass spectroscopy using rotating cylinder electrode technique. They proposed the following reaction mechanism:

$$CO_2 \longrightarrow CO_{ad} \longrightarrow CH_{2ad} \longrightarrow CH_4 \text{ or } C_2H_4$$

and possible side reaction:

$$CO_2 \longrightarrow CHOO \longrightarrow C$$

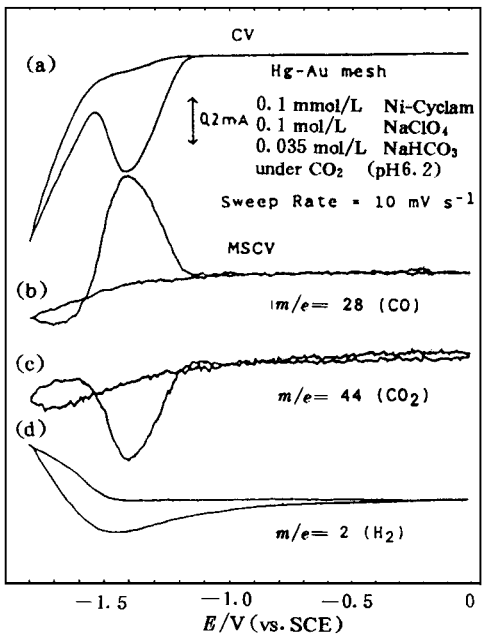

Fig. 3　Cyclic voltammogram (a) and MSCV results for (b) CO, (c) CO_2, as well as (d) H_2. Sweep rate: 10 mV·s^{-}

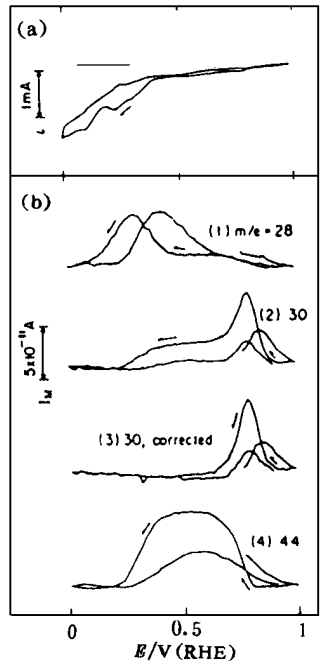

Fig. 4　Current vs. Potential curve (a) obtained on a porous Pt electrode in 0.5 mol/L H_2HO_4 solution containing 1.2×10^{-2} M $NaNO_2$, sweep rate: 1 mV·s^{-1}. (b) Mass current vs. potential curves for (1) $m/e = 28$ (N_2^+), (2) 30 (NO^+), (3) 30 but after subtracting from curve 2 the NO^+ fragment derived from N_2O in curve 4, and (4) 44 (N_2O^+)

In addition, *in situ* analysis of products in electroreduction of CO_2 with Ni-Cyclam by DEMS on CV at a Hg-Au mesh electrode gave a clear observation as shown in Figure 3 where the steep rise in cathodic current was attributed to hydrogen evolution because the same steep rise was also observed on CV under N_2 in the same solution[12].

1.3　HCOOH electrooxidation and O_2 evolution

In general, it is believed that formic acid was oxidized on Pt in a dual path mechanism. Wolter and Heitbaum[13], using ^{18}O labelling and DEMS method, which offers the unique advan-

tages of the on-line monitoring the volatile products and discriminating between different reaction pathways, obtained a direct evidence for the dual path mechanism, where the "reactive intermediate" had been suggested to be $COOH_{ad}$ and the "inhibiting intermediate" HCO_{ad}. On the condition of ^{18}O-labelled formic acid in $H_2{}^{16}O$, the ^{18}O-labelled intermediate was oxidized to $CO^{18}O^{16}$ by a three-electron process in $H_2{}^{16}O$, and direct oxidation of $HC^{16}O^{16}OH$ in $H_2{}^{18}O$ formed $C^{16}O^{16}O$. Another example using ^{18}O labelling together with DEMS is the study on oxide layer formation and O_2 evolution on Ru and RuO_2 film in sulphuric adic[14]. It was directly shown that the oxide layer took part in the oxygen evolution process on both types of electrode. On the Ru electrode, the formation of RuO_4 was observed when oxygen evolution took place.

1.4 NO_2^- of NO_3^- electroreduction

The electroreduction of NO_2^- (or HNO_2) and NO_3^- has received a considerable attention because of their contribution to air pollution. The reaction products and the mechanisms had not been sufficiently clarified. With the help of DEMS technique, Nishimura et al[15] detected the volatile products of the electroreduction of NO_2^- and NO_3^- at Pt in H_2SO_4 and found nitrite was gradually reduced to NO(0.6～1.0 V, vs. RHE), N_2O (0.2～0.8 V) and N_2(0.1～0.6 V) in the potential ranges indicated in Figure 4, and nitrate was reduced to N_2O and N_2 simultaneously and transiently at potentials lower than 0.4 V but there was no NO formed.

1.5 CO Adsorption and electrooxidation

In addition, the application of DEMS technique can be also found in other research fields, the behaviours of adsorption and oxidation of CO at Pt electrode were described in the literatures[16,17] by using DEMS. It is of interest to note that a quantitative correlation in the electroxidation of CO_{ad} could be achieved between the faradaic current of the electrochemical desorption process and the mass intensity of the desorption product simultaneously measured with DEMS by Wolter and Heitbaum[16]. With the help of the method, they found two kinds of adsorbed CO, but did not observe the existence of "reduced" CO at Pt electrode. For the strongly bound intermediate of small organic molecules, such as formic acid, methanol as well as ethanol, their evidence of the intermediate species and the structure of the adsorbate have been also directly obtained by DEMS together with isotope labelling[18].

1.6 Unsaturated hydrocarbon electroreduction

There were lots of publications on DEMS studies of unsaturated hydrocarbons such as C_2H_2, C_6H_6 and so on, at Pt single crystal electrodes in recent years[19～23]. Kita and GAO investigated electroreduction of acetylene(C_2H_2) at Pt single crystal electrodes in H_2SO_4 solution[23] and observed that Pt(110) showed the best catalyst for the reaction of C_2H_2 with H, which mainly produced C_2H_2 with a small part of C_2H_6 as shown in Figure 5. The electrochemical reactivity of Pt(100) electrode lies between Pt(110) and Pt(111) for the hydrogenation of acetylene. Baltr-

uschat and co-workers discussed the electrochemical behaviour of benzene(C_6H_6) at Pt, Rh and Pd single crystal electrodes in H_2SO_4 solution by DEMS measurements[19~21]. It is obvious that desorption from Pt(111) electrode mainly produced benzene itself, whereas all adsorbed benzene molecules of Pt(110) were hydrogenated to cyclohexane. Less than a half of the adsorbate on Pt(100) was desorbable at the negative potentials. Hydrogenating desorption of the benzene adsorbate decreased in the order of Pt > Rh > Pd.

2 Summary

The applications of the DEMS method have been found in some electrochemical processes, such as reactions of CH_3OH, HCOOH, NO_2^- (or NO_3^-), CO_2, CO, O_2 as well as unsaturated hydrocarbon at the different kinds of electrodes. It is very promising for the further studies and *in situ* analysis on intermediate species, structure properties of intermediates andcompositions of the faradaic efficiencies in a quantitative manner for the concomitant generation of gases as a function of electrode potential or time during the electrochemical reaction by the method of the DEMS technique.

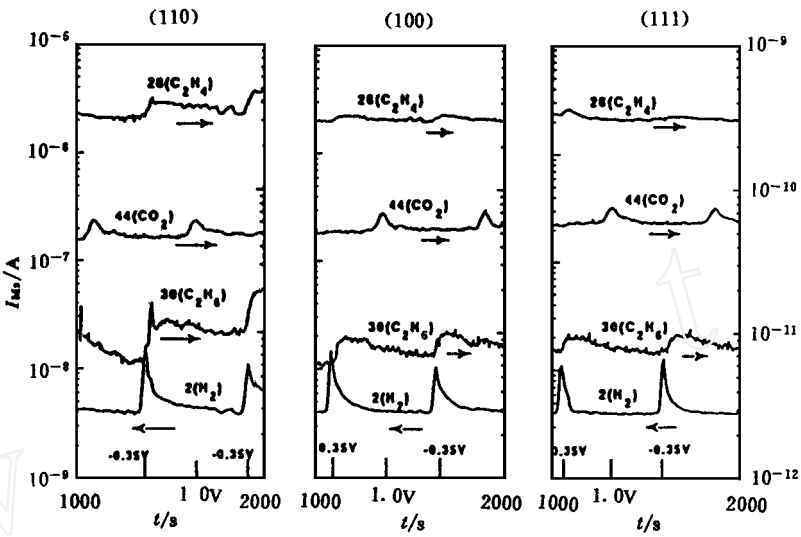

Fig. 5　Mass signals as function of time for the products of the acetylene electroreduction on Pt single crystal electrodes in 0.5 M H_2SO_4, scan rate: 10 mV·s^{-1}

Key words　Electrooxidation, Electroreduction, Adsorption, Intermediate

References

1　Lamy C, Legar J M, Clavilier J et al. *J. Electroanal. Chem.*, 1983, 150: 71
2　Bagotzky V S, Vassiliev U B Khazova O A. Generalized schem of chemisorption electrooxidation and electroreduction of simple organic compounds on platium group metals. *J. Electroanal. Chem.*, 1977, 81: 229
3　Wieckowski A, Sobkowski J, Szamre I. *J Rocz. Chem.*, 1974, 48: 77
4　Breiter M E, Electrochemical Processes in fuel Cills. Berlin: Springer Verlag, 1969
5　Beden B, Lamy C, Bewick A et al. Electrosorption of methanol on a platium electrode IR spectroscopic evidence for adsorbed CO species. *J. Electroanal. Chem.*, 1981, 121: 343
6　Bittins-Cattaneo B, Iwasita T. Electrocatalysis of methanol oxidation by adsorbed Tin on Pt. *J. Electroanal.*